

PATENT SPECIFICATION

(11) 1390503

1390503

- (21) Application No. 8132/71
- (22) Filed 30 March 1971
- (23) Complete Specification filed 29 March 1972
- (44) Complete Specification published 16 April 1975
- (51) INT CL² C11D 11/00
- (52) Index at acceptance

CSD 6A2 6A3 6A4B 6A5C 6A5D1 6A5D2 6A5E 6A9
 6B10A 6B10B 6B11A 6B11B 6B11C 6B12B1 6B12B2
 6B12F2 6B12G2A 6B12G2B 6B12G6 6B12K2
 6B12L 6B12N2 6B13 6B15 6B1 6B2 6B4 6B6 6B7
 6B8 6C7 6C8 6D

(72) Inventors JEFFREY DALE HAMPSON
 IAN ROGER KENYON and
 MICHAEL DAVID RICKARD



(54) LIQUID DETERGENT COMPOSITIONS

5 (71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E.C.4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a liquid aqueous detergent composition containing capsules which are insoluble in the composition, but which release their contents when the composition is diluted with water.

15 Detergent compositions containing capsules in a liquid environment are known in which the capsules are insoluble but release their content on mechanical rupture, or on melting with an increase in temperature when the 20 compositions are used. The present invention is concerned with detergent compositions containing capsules which release their contents according to a new principle, namely that on dilution of the composition with 25 water, the change in ionic strength of the liquid environment of the capsules enables the encapsulation material in the capsules to dissolve.

30 The present invention provides an aqueous detergent composition comprising a liquid aqueous medium containing from 1 to 50% by weight of an organic detergent-active material and at least 1% by weight of a non-detergent electrolyte, and, suspended in the 35 medium, capsules containing core material and having at their surface water-soluble polymer gel, in which the electrolyte and its concentration in the medium, and the polymer gel are such that the polymer gel is insoluble in the medium, but dissolves with release of the core material when the 40 composition is diluted with water. Preferably the composition comprises from 20 to 99.9 parts

by weight of liquid aqueous medium and form 80 to 0.1 parts by weight of capsules.

45 A liquid aqueous medium includes, both a normally liquid medium and a gelled aqueous liquid medium that is mobile when stress is applied.

50 Suitable organic detergent-active materials are anionic surface-active agents, for example, an alkali metal or ammonium salt of an alkyl-aryl sulphonic acid, of an alphaolefin sulphonic acid, or of a sulphate monoester of a polyethoxylated alkanol; nonionic surface-active agents, for example a fatty acid ethanolamide; a polyethoxylated alkanol or a polyethoxylated alkylphenol; and cationic surface-active agents, for example a dialkyl-dimethylammonium chloride where the alkyl groups are long chain alkyl groups. A detergent-active material that interferes with the function of the polymer gel, for instance by formation of a water-insoluble complex, will of course not be used.

55 By non-detergent electrolyte is meant a water-soluble ionisable salt having an inorganic anion and an inorganic cation or a cation from an organic acid, but excluding detergent-active compounds. Examples of such organic acids are acetic, propionic, acrylic chloracetic, dichloracetic, trichloracetic, lactic, pyruvic, oxalic, succinic, maleic, fumaric, citric, tartaric, malic, citraconic, and itaconic acids. Preferably the electrolyte is an alkali metal or ammonium chloride, sulphate, pyrophosphate, tripolyphosphate or dihydrogen orthophosphate, or an alkali metal or ammonium citrate.

60 70 75 80 85 A capsule can consist of a core material surrounded by a wall of polymer gel, or the core material can be mixed with the polymer gel which provides at the capsule surface an effective encapsulation for the core material. Preferably the polymer gel forms a wall surrounding the core material, and preferably

the capsules contain from 2 to 30% by weight of polymer gel. The core material can be solid or liquid. A capsule can be formed from a homogeneous mixture of polymer and core material and this form is particularly useful where it is desired to release only very small quantities of an active substance, for example a bactericidal agent, when the composition is used. A core material can be a material that is unstable in the liquid aqueous medium, or would if released create instability in it, for instance a bleaching agent or solvent. Examples of other suitable core materials are cosmetic emollients, detergent-active materials, foam boosters, bactericidal agents, fluorescers and perfumes. Core material will be released from a capsule when the polymer gel dissolves on dilution and the delay that occurs during the dissolving process before release, for instance of further detergent, can be used to improve the performance of the composition.

The polymer gel must be stable to the liquid aqueous medium and to the core material. It is sufficiently water-soluble for substantially complete solution to occur in water at 40-45°C within 15 minutes with

30
35
40
45
50

55

	Polymer	polymer concentration g/100 ml	Minimum sodium sulphate concentration g/100 ml inducing precipitation at		
			0°C	25°C	50°C
60	Polyvinyl alcohol A (99% hydrolysed PVA, 30 cP)	10	6.0	4.5	3.0
	Polyvinyl alcohol B (99% hydrolysed PVA, 5 cP)	10	7.0	5.0	4.0
65	Polyvinyl alcohol C (88% hydrolysed PVA, 42 cP)	10	6.0	3.5	2.0
	Methylcellulose (25 cP)	5	6.5	5.0	2.5
	Hydroxypropylcellulose (50 cP)	5	6.0	6.0	2.0

An alternative test that can be used involves the casting of a film of the polymer. A glass slide is dipped in an aqueous solution of suitable polymer concentration, conveniently of viscosity 20 poise or less and is allowed to dry freely in air, then evaporated to dryness in a vacuum oven. The slides are immersed in a test solution, such as 20% aqueous sodium sulphate, 30% aqueous sodium citrate or 30% aqueous sodium tartrate, and allowed to stand at ambient temperature for 3 days. Films which remain in completely coherent gel form over the surface of the slide are of suitable polymers.

Suitable polymer gels can be chosen from polysaccharides, especially carrageenan, guar gum, alginic acid and amylopectin, and pectins such as low methoxy amide pectin and low methoxyl citrus pectin; a partially acetylated xanthan gum; cellulose ethers, for example methyl, hydroxyethyl, hydroxypropyl and carboxymethyl cellulose; synthetic polymers, for example polyvinyl alcohol obtained

agitation, but is insoluble in liquid aqueous media of the chosen electrolyte concentration. Suitable polymer gels are those that are insoluble in 20% by weight aqueous sodium sulphate, 30% by weight aqueous sodium citrate or 30% by weight aqueous sodium tartrate solution. Whether a particular polymer is suitable at a given electrolyte concentration can readily be determined by testing. For instance 0.5 ml samples of a dilute aqueous solution of the polymer under test can be added to 10 ml quantities of solutions containing sodium sulphate in a series of concentrations within the range 0.5 to 20 g/100 ml. A polymer that readily forms a coherent gelatinous precipitate is suitable, and polymers which forms the precipitate with concentrations of 10 g/100 ml or less sodium sulphate at 0°, 25° and 50°C are particularly suitable, for example, the following polymers, in which the polyvinyl alcohols are polymers prepared by the hydrolysis of polyvinyl acetate and have degrees of hydrolysis and viscosities in 4% aqueous solution at 20°C as indicated, and the cellulose derivatives have viscosities in 2% aqueous solution at 20°C as indicated.

30

35

40

45

50

by hydrolysis of polyvinyl acetate, polyacrylic acid, and polyethylene oxide; and gelatin, for example of isoelectric point 5.5 to 6, 7 to 8, and 8.

Capsules can be of size down to 1 micron in diameter but preferably they are large enough to be visible as discrete entities: a capsule can for example have its largest dimension within the range from 500 to 4000 microns. Capsules of from 500 to 4000 microns diameter can be made by a variety of processes, for example by co-extrusion of liquid core material and dilute aqueous solution of non-gelled polymer wall material from a nozzle having concentric orifices; by centrifugal extrusion of "rods" of liquid core material sheathed in the liquid wall material; by rotating discs in which a membrane of wall material is formed across an orifice to envelope the liquid core material; and by bi-liquid column ejection. The co-extrusion process is preferable, and where a solution of polymer is extruded, it can be dehydrated

90

95

100

105

110

- and gelled rapidly in a collecting bath selected according to the gelation characteristics of the polymer. Gelation can be effected by the action of a dissolved salt, for example sodium sulphate, with or without an alcohol, in the bath. Gelation can be accelerated by heating the collecting bath and by including a chemical cross-linking agent in it. Where a chemical cross-linking agent, for example borate, is used, the degree of cross-linking should be carefully controlled, in order to avoid making the polymer gel insoluble on dilution. Alternatively the extruded material can be dried by hot gas, to remove the water by evaporation.
- Where the core material is a liquid, it should preferably be of similar density to that of the polymer solution from which the capsule wall is formed. It should have a viscosity in the range from 200 to 900 cp. Control of viscosity and density is advantageous as it greatly assist centralisation of the core before the polymer gels. Control of density is also important, because as described in British Patent 1,303,810, there are practical limits of density difference between the capsules and a liquid medium in which they are to be suspended. Examples of liquid core materials whose viscosity and density is controlled by additives are perfumes, for instance lemon oil, to which titanium dioxide is added for density control; non-polar solvents, for instance chloroform, to which liquid paraffin is added to control viscosity and density; and aqueous surfactant solutions, to which ethylene glycol is added to control viscosity and density.
- Chemical methods of encapsulation, such as coacervation, organic phase separation and interfacial polymerisation, are not generally suitable for the production of capsules of at least 500 micron diameter and are best utilised for capsules of up to 150 microns.
- Capsules can also be prepared by marumerisation, in which powdered core material is converted to a plastic mass using water or other solvent in conjunction with a binder, and the mass is extruded under pressure through a perforated die. The cylindrical extrudate is placed in a marumeriser machine in which it is broken down until cylinders of length equal to their diameter are produced, and rolled into spheres by centrifugal and frictional forces. The spheres are then coated in the marumeriser by continuous addition of a dilute aqueous solution of the water-soluble polymer that is to provide the polymer gel. The water is simultaneously evaporated off, assisted by a current of hot air, and this is continued until the sphere has been encapsulated by polymer gel.
- The electrolyte can have other functions than stabilising the capsule in the medium; for instance it can be a builder for the detergent-active material. Choice of electrolyte can depend on the temperature conditions expected in the storage and transportation of the composition, for at lower temperatures some electrolytes may be insufficiently soluble and crystallise out, thus failing to maintain the capsule stability. In the choice of a polyvalent cation or anion electrolyte, care should be taken that irreversible cross-linking of the polymer gel is avoided. Thus if a calcium ion is present in the electrolyte, an alginate should not be selected for the polymer, because interaction between these is not reversible on dilution.
- The liquid aqueous medium can also contain ingredients such as perfumes, dyes, sequestrants and hydratropes, and dispersed insoluble constituents other than the capsules.
- In compositions of the invention, the capsules are suspended in the liquid aqueous medium, preferably in such a way that they maintain their spatial position during storage. Where the liquid aqueous medium is required to have such suspending properties, it preferably maintains the capsules in suspension by surfactant micellar interaction, for example as described in British Patents 882,569, 955,081, 1,262,280 and 1,308,190. The liquid aqueous medium can contain an inorganic or polymeric organic structuring agent which maintains the capsules in suspension: there are many such materials whose use for giving a liquid suspending properties is well known, for example natural or synthetic montmorillonite clays and carboxyvinyl polymers. The method of suspending capsules should take into account the electrolyte content of the liquid aqueous medium; for compositions requiring a high electrolyte content, micellar interaction to achieve suspending power may not be a possible. It is preferable to select a medium which is clear, for the aesthetic appeal of the composition.
- Compositions useful as heavy-duty liquid compositions for fabric washing are those whose liquid aqueous media contain from 1 to 15% by weight of organic detergent-active material and from 20 to 30% by weight of an alkaline builder salt as electrolyte, for example an alkali metal pyrophosphate, tripolyphosphate, citrate, or silicate.
- Dishwashing liquids, shampoos, and bath products have little builder salt content, and for these electrolyte is used in amounts of from 3 to 10% by weight of the aqueous medium. A typical dishwashing liquid contains from 20 to 45%, and a typical bath product or shampoo contains from 5 to 30%, by weight of organic detergent-active material. In these products having from 5 to 45% by weight of detergent-active material and from 3 to 10% by weight of electrolyte, capsules whose polymer gel is carageenan,

polyvinyl alcohol or a cellulose ether are particularly suitable. With detergent liquids containing only 1 to 3% by weight of electrolyte, carageenan is suitable as polymer gel.

- 5 The invention is illustrated by the following Examples, in which temperatures are in °C and amounts are by weight.

EXAMPLE 1

10 Capsules consisting of an aqueous solution of 50% sodium lauryl triethoxysulphate and 16.7% ethylene glycol as liquid core material encapsulated in polyvinyl alcohol gel from an aqueous solution of 6.7% of a polyvinyl alcohol obtained by 88% hydrolysis of PVA and whose 4% solution had a viscosity of 22 cp at 20°, 3.3% of a polyvinyl alcohol obtained by 88% hydrolysis of PVA and whose 4% solution had a viscosity of 5 cp at 20°, and 0.0005% boric acid, were prepared using a concentric orifice extruder constructed as described in US Patent 1,799,897. The core material was fed through a capillary tube to a nozzle held in the centre of an outer orifice from which the wall material was extruded. The capillary nozzle and outer orifice, of a size selected to give 4000 micron diameter capsules, were arranged so as to form a type of needle valve which forced the wall material to flow around and below the capillary nozzle. By adjusting the flow rate of the two materials fluid droplets consisting of a thin shell of wall material filled with core material were formed below the two orifices, and these droplets were allowed to fall into a collecting bath consisting of an aqueous solution of 0.5% sodium hydroxide and 20% sodium sulphate. Polymer gel was formed due to the effect of the sodium sulphate, supplemented by the cross-linking effect of borate ions.

30 The resulting capsules were spheroidal, of volume 0.033 ml and density 1.15, and contained 75% of core material.

40 The capsules were immediately incorporated at a level of 3 capsules per ml in a dishwashing liquid aqueous medium of density 1.12 and yield value 2 to 3 dyne/cm², having the following composition.

	%
50 Sodium dodecylbenzene sulphonate	23.5
Cocomonoethanolamide	5
Sodium sulphate	8.5
Sodium xylene sulphonate	7
Synthetic hectorite clay (5% aqueous dispersion)	30
Water, perfume and dye to	100

55 The capsules were quite stable in this liquid, they did not disperse and remained suspended during storage of the product at 50°, 0° and after freeze-thaw cycling between -15° and 10°.

60 After storage for 3 days, 2 ml of the com-

position was dissolved in 1000 ml water, simulating dilution for dishwashing. The gel slowly dissolved in water at 45°, to release the core material in about 7 minutes. Dishwashing tests with soiled plates demonstrated that the detergent-active material released from the capsules significantly contributed to the number of plates which could be washed before the foam on the surface of the washing solution collapsed.

EXAMPLE 2

7 A suspension of 25% titanium dioxide in lemon oil as core material was encapsulated in a methylcellulose gel prepared as described in Example 1 from a 5% aqueous solution of a methylcellulose having in 2% aqueous solution a viscosity of 25 cp at 20°, using a capillary nozzle and outer orifice of size selected to give 3000 micron diameter capsules. The collecting bath was 20% aqueous sodium sulphate; and taking advantage of the unusual property of methylcellulose gels to dehydrate further with increase of temperature gel formation was accelerated by raising the temperature of the bath to 70°.

8 The resulting spheroidal capsules were of volume 0.014 ml and density 1.15, and contained 75% of core material.

9 The capsules were incorporated at a level of 1 capsule per ml in a liquid aqueous medium of density 1.05, and of the following composition:

	%
Sodium lauryl triethoxysulphate	13.3
Sodium dihydrogen orthophosphate	7
Lauryl alcohol	4.3
Dibutyl phthalate	3
Ethanol	18.0
Water and dye to	100

10 This medium possessed suspending properties by surfactant micellar interaction as described in British Patent 1,308,190, and had a yield value of 3.5 dyne/cm².

11 The composition exhibited good storage properties under the conditions described in Example 1. The capsules released their core material within 1 minute when diluted in bath water, to give a lemon fragrance.

EXAMPLE 3

12 Liquid paraffin as core material was encapsulated in a 3% aqueous solution of a sodium carboxymethylcellulose having in 2% solution a viscosity of 40 cp at 20° as described in Example 1, with an orifice selected to give 2000 micron diameter capsules. The collecting bath was an 8% aqueous solution of aluminium sulphate which effected gelation both by salting out and cross-linking the carboxyl groups with aluminium ions. The resulting capsules were spheroidal, of

volume 0.004 ml and density 1.08, and contained 60% of core material.

The capsules were incorporated at a level of 50 capsules per ml in a liquid aqueous medium of the following composition and having a density of 1.12 and yield value of 1 to 2 dyne/cm².

	%
10	Sodium lauryl triethoxysulphate
	15
10	Nonylphenol-12 ethylene oxide condensate
	10
	Ethyl alcohol
	2
15	Synthetic hectorite clay (5% aqueous dispersion)
	30
15	Sodium sulphate
	5
	Water, dye and perfume to
	100

The composition was suitable as a shampoo, the encapsulated liquid paraffin acting as a cosmetic emollient and as an agent for improving the manageability of hair upon release. The contents of the capsules were released by polymer gel dissolution on dilution in less than 15 minutes.

EXAMPLE 4

A suspension of 15 parts of titanium dioxide and 12 parts of a dianilinodiethanol-aminostilbene cotton fluorescer in 73 parts of liquid paraffin as core material was encapsulated in a polymer gel prepared from a 5% solution of high strength acid gelatin (isoelectric point 7 to 8) as described in Example 1 and using a capillary nozzle and outer orifice selected to give 1000 micron diameter capsules. The encapsulating solution was held at 35° to prevent it gelling in the extruder, and the collecting bath was 20% aqueous sodium sulphate at ambient temperature.

The resulting spheroidal capsules of volume 0.0095 ml and density 1.15 contained 95% of core material. The capsules were incorporated at a level of 16 capsules per ml in a liquid aqueous medium of density 1.05 and the following composition.

	%
15	Sodium dodecylbenzene sulphonate
	10
	Potassium tripolyphosphate
	20
	Lauric diethanolamide
	3.5
10	Potassium xylene sulphonate
	7.5
10	Sodium carboxymethyl cellulose
	1
	Alkaline sodium silicate (48% aqueous solution)
	5
15	Synthetic hectorite clay (5% aqueous dispersion)
	30
15	Water to
	100

The resulting composition containing about 0.1% fluorescer was used in a wash solution to which hypochlorite bleaching agent was also added. At a solution temperature of 60°, the capsules released their

contents about 5 minutes after the start of the washing operation, then the bleaching agent had decomposed, and the fluorescer was thus protected from attack by the bleaching agent. The product could be packed in a transparent container without risk of photochemical decomposition of the fluorescer.

65

EXAMPLES 5 and 6

Compositions were prepared as in Example 4 but using potassium pyrophosphate (Example 5) and sodium citrate (Example 6) respectively instead of potassium tripolyphosphate. The capsules released their contents within 5 minutes at 60°, and within 7 minutes at 40 to 45°.

70

EXAMPLES 7 to 10

Compositions were prepared as in Example 4 but with the gelatin replaced respectively by a polyethylene oxide of molecular weight 2×10^5 (Example 7); a partially acetylated xanthan gum (Example 8); a low methoxy amide pectin (Example 9); and a low methoxyl citrus pectin (Example 10). Core material was released from the capsules on dilution within 5 minutes at 60° and within 4 minutes at 40 to 45°.

80

EXAMPLE 11

Capsules were produced as described in Example 1, using a capillary nozzle and outer orifice selected to give 4000 micron diameter capsules, and using as core material 10 parts titanium dioxide and 6 parts of tribromosalicylanilide dispersed in 84 parts of liquid paraffin, and an encapsulating solution consisting of 1% kappa-carrageenan, 2% iota-carrageenan, 0.25% locus bean gum, 2% glycerol and 94.5% water. The extrusion equipment was heated to 70° in order to avoid gelation and the collecting bath consisted of 75% alcohol, 20% water and 5% potassium chloride and was maintained at ambient temperature.

90

The resulting spheroidal capsules of volume 0.033 ml and density 1.05 contained 95% of core material. They were incorporated at level of 1 capsule per ml in a clear dishwashing liquid of density 1.05 and the following composition.

95

	%
	Sodium alkylbenzene sulphonate
	20
	Sodium C ₁₄₋₁₆ alpha-olefin sulphonate
	5
	Lauric diethanolamide
	5
	Sodium xylene sulphonate
	7
	Ethyl alcohol
	3
	Potassium chloride
	1
	Synthetic hectorite clay (5% aqueous dispersion)
	20
	Sodium ethylenediamine tetraacetate
	0.2
	Water to
	100
	120

100

105

110

115

This composition was physically stable for at least 3 months in a temperature range of 0 to 35°. Because of the protection afforded by encapsulation, the tribromo-
5 salicylanilide exhibited no tendency to dis- coloration when the product was packed in a clear containers and subjected to prolonged exposure to daylight.

When used as a dishwashing product the 10 capsules released the core material within 2 minutes at a washing solution temperature of 45°.

EXAMPLE 12

The capsules of Example 11 were incor- 15 porated as described in Example 11 in a liquid aqueous medium of the following com- position.

		%
20	Sodium lauryl triethoxysulphate	18
	Lauryl alcohol	2.7
	Ammonium chloride	9.0
	Dibutyl phthalate	1.8
	Ethyl alcohol	13.0
	Water to	100

25 This liquid aqueous medium possessed suspending properties by surfactant micellar interaction as described in British Patent 1,308,190. The capsules released their core material in under 4 minutes when diluted 30 with water at 40 to 45°.

WHAT WE CLAIM IS:—

1. An aqueous detergent composition comprising a liquid aqueous medium containing from 1 to 50% by weight of an organic 35 detergent-active material and at least 1% by weight of a non-detergent electrolyte, and, suspended in the medium, capsules containing core material and having at their surface a water-soluble polymer gel, in which the 40 electrolyte and its concentration in the medium, and the polymer gel are such that the polymer gel is insoluble in the medium, but dissolves with release of the core material when the composition is diluted with water.
- 45 2. A composition according to Claim 1, where the polymer gel forms a well surrounding the core material.
3. A composition according to Claim 2, in which the capsules contain from 2 to 30% 50 by weight of polymer gel.
4. A composition according to any preceding claim, comprising from 20 to 99.9 parts by weight of liquid aqueous medium and from 80 to 0.1 parts by weight of capsules.
- 55 5. A composition according to any preceding claim, in which the polymer gel is a polysaccharide.
6. A composition according to any one of Claims 1 to 4, in which the polymer gel is 60 a cellulose ether.

7. A composition according to any one of Claims 1 to 4, in which the polymer gel is polyvinyl alcohol, polyacrylic acid or a polyethylene oxide.

8. A composition according to any one of Claims 1 to 4, in which the polymer gel is 65 gelatin.

9. A composition according to any preceding claim, in which the liquid aqueous medium contains an inorganic or polymeric organic structuring agent which maintains the capsules in suspension.

10. A composition according to any one of Claims 1 to 8, in which the liquid aqueous medium maintains the capsules in suspension by surfactant micellar interaction.

11. A composition according to any preceding claim, in which the aqueous medium contains from 1 to 15% by weight of organic detergent-active material and from 20 to 30% by weight of an alkaline builder salt.

12. A composition according to any one of Claims 1 to 10, in which the aqueous medium contains from 3 to 10% by weight of the electrolyte.

13. A composition according to Claim 12, in which the aqueous medium contains from 5 to 45% by weight of organic detergent-active material.

14. A composition according to Claim 13, in which the polymer gel is carrageenan, polyvinyl alcohol or a cellulose ether.

15. A composition according to any preceding claim, in which the electrolyte comprises an alkali metal or ammonium chloride or sulphate.

16. A composition according to any one of Claims 1 to 14, in which the electrolyte comprises an alkali metal or ammonium pyrophosphate, tripolyphosphate or dihydrogen orthophosphate, or an alkali metal or ammonium citrate.

17. A composition according to any preceding claim, in which the core material comprises a bleaching agent, solvent, perfume, cosmetic emollient, bactericidal agent, fluorescer, foam booster or detergent-active material.

18. A composition according to any preceding claim, in which the capsules have a largest dimension of from 500 to 4000 microns.

19. A composition according to Claim 1, substantially as described in any one of Examples 1 to 3.

20. A composition according to Claim 1, substantially as described in any one of Examples 4 to 12.

G. H. HARGREAVES,
Chartered Patent Agent.